

PATENT ABSTRACTS OF JAPAN

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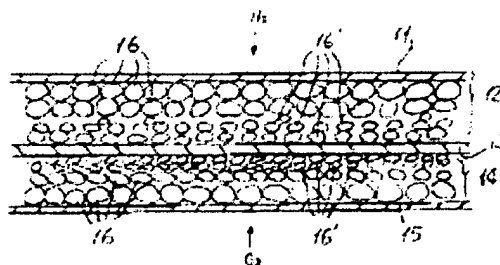
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(54) POLYMER ELECTROLYTIC ELECTROCHEMICAL CELL AND ITS MANUFACTURE

(57)Abstract:

PURPOSE: To provide a polymer electrolytic electrochemical cell capable of improving gas permeability and developing high power.

CONSTITUTION: The grain size of agglomerated catalyst grains 16, 16' in at least one of both catalyst layers of an electrochemical cell with an anode collector 11, an anode catalyst layer 12, a polymer electrolytic coat 13, a cathode catalytic layer 14 and a cathode collector 15 layered in sequence are distributed gradually smaller as tending toward the polymer electrolytic coat and gradually larger as tending toward the collector. On the side nearer the collector, gas permeability has priority, and on the side nearer the polymer electrolytic coat, the use factor of catalyst is considered important. The best gas permeability and the best use factor of the catalyst is thus obtained in such distribution.



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CLAIMS

[Claim(s)]

[Claim 1] It laminates in order of an anode charge collector-anode catalyst layer-polymer-electrolyte-membrane-cathode catalyst bed-cathode charge collector. In a catalyst bed of an electrode for polymer electrolyte type electrochemical cells which formed in layers cluster particles which grow into catalyst support from a catalyst particle and ion-exchange resin which supported a catalyst, A polymer electrolyte type electrochemical cell distributing said catalyst particle so that particle diameter of said cluster of a small side near a charge collector may become large about particle diameter of said cluster of a side near polymer electrolyte membrane of at least one catalyst bed.

[Claim 2] It laminates in order of an anode charge collector-anode catalyst layer-polymer-electrolyte-membrane-cathode catalyst bed-cathode charge collector. In a catalyst bed of an electrode for polymer electrolyte type electrochemical cells which formed in layers cluster particles which grow into catalyst support from a catalyst particle and ion-exchange resin which supported a catalyst, A polymer electrolyte type electrochemical cell distributing said cluster particle so that it may become low about concentration of ion-exchange resin of a high side near a charge collector in concentration of said ion-exchange resin of a side near polymer electrolyte membrane of at least one catalyst bed.

[Claim 3] It laminates in order of an anode charge collector-anode catalyst layer-polymer-electrolyte-membrane-cathode catalyst bed-cathode charge collector. In a manufacturing method of a catalyst bed of an electrode for polymer electrolyte type electrochemical cells with which both catalyst beds formed in catalyst support in layers cluster particles which comprise a catalyst particle and ion-exchange resin which supported a catalyst, After carrying out natural sedimentation filtration of the dispersion liquid of a catalyst particle cluster made to cover or adsorb ion-exchange resin on at least one charge collector of each on this charge collector, A manufacturing method of a polymer electrolyte type electrochemical cell laminating in order of an anode charge collector-anode catalyst layer-polymer-electrolyte-membrane-cathode catalyst bed-cathode charge collector.

[Claim 4] It laminates in order of an anode charge collector-anode catalyst layer-polymer-electrolyte-membrane-cathode catalyst bed-cathode charge collector. In a manufacturing method of an electrode for polymer electrolyte type electrochemical cells which comprises a catalyst bed which formed in layers cluster particles which grow into catalyst support from a catalyst particle and ion-exchange resin which supported a catalyst, Produce several cluster particles from which ion-exchange resin concentration differs, laminate in layers cluster particles which have ion-exchange resin of maximum concentration in order with high concentration from said polymer-electrolyte-membrane side, and at least one catalyst bed is constituted, A manufacturing method of a polymer electrolyte type electrochemical cell laminating in order of an anode charge collector-anode catalyst layer-polymer-electrolyte-membrane-cathode catalyst bed-cathode charge collector.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention makes easy supply of reactant gas, and discharge of production gas, and relates to a polymer electrolyte type electrochemical cell which raised the marginal output obtained in a practical use region, and a manufacturing method for the same.

[0002]

[Conventional technology and a problem] Since a polymer electrolyte type electrochemical cell, for example, a fuel cell, can take out compact and high current density as compared with a phosphoric acid fuel cell, it attracts attention as an electromobile and a power supply for spacecrafts. Also in development of this field, the proposal about various electrode structures, a catalyst manufacturing method, a system configuration, etc. is made. Drawing 1 is what shows typically the principle and composition of a polyelectrolyte type fuel cell, The anode side gas diffusion electrode 4A of the ion-exchange membrane 1 which, on the other hand, joins the anode side porous catalyst layer 2A and the anode side water repellence porous collector layer 3A to a field, moreover -- on the other hand -- being alike -- the cathode side gas diffusion electrode 4C which joins cathode side water repellence porous collector layer 3C to the cathode side porous catalyst layer 2C is joined. The separator 6A which has the reactant gas supply groove 5A touches the gas diffusion electrode 4A by the side of an anode, and the collecting section 7A is formed between the supply grooves 5A of this separator 6A. The separator 6C which has the reactant gas supply groove 5C touches the gas diffusion electrode 4C by the side of a cathode similarly, and the collecting section 7C is formed between the supply grooves 5C of this separator 6C. Between both the collecting sections 6A and 46 is connected with the lead which has the load 8, and if hydrogen is supplied to the anode side and oxygen is supplied to the cathode side, electric power can be taken out from said load 8.

[0003]A carbon particle is used as a carrier of the electrode catalyst layer of such an electrode for electrochemical cells, this carbon particle and ion-exchange resin are mixed, it binds with a hotpress etc., and an electrode catalyst layer is formed. Since it fills up with the electrode catalyst layer formed in this way without a crevice since a carbon particle is a globular form, and it moreover sticks firmly mutually with a hotpress and density is high, There are few circulation ways of gas, therefore material gas diffuses the inside of an electrode catalyst layer, and there is a fault of it being hard to reach a reactive site being further hard to perform discharge of the production gas after a reaction smoothly. Therefore, it becomes further difficult to perform supply of material gas, the reaction efficiency in the electrode catalyst layer fell substantially, and the problem that only the energy which is much less than the theoretical maximum output can be taken out has arisen.

[0004]

[Objects of the Invention]An object of this invention is to provide an electrode for polymer electrolyte type electrochemical cells from which the maximum output is obtained, and a manufacturing method for the same, while performing smoothly supply of reactant gas, and discharge of production gas in view of the above-mentioned problem.

[0005]

[Means for Solving the Problem] This invention is so large that it approaches the charge collector side in particle diameter of a cluster which a catalyst of a polymer electrolyte type electrochemical cell which laminates a charge collector, a catalyst bed, and polymer electrolyte membrane condensed. They are a polymer electrolyte type electrochemical cell which made so large [it is so small that the charge collector side is approached, and] that the polymer-electrolyte-membrane side is approached concentration of ion-exchange resin which makes it so small that the polymer-electrolyte-membrane side is approached, or covers said catalyst, and a manufacturing method for the same.

[0006] Hereafter, details of this invention are explained. This invention means performing smoothly supply of reactant gas and discharge of production gas which are performed [1st] through a catalyst bed, and means 2nd promoting a reaction between anode gas and cathode gas. Although a catalyst bed comprises much catalyst particles and ion-exchange resin which supported a detailed catalyst to catalyst support, a catalyst particle is condensed mutually and forms a cluster (floc). Space which is got blocked, so that the degree of condensation is large, and is formed between clusters, so that particle diameter of a cluster is large becomes large, it becomes difficult to expose a catalyst supported by catalyst particle on the other hand to this space, and a capacity factor of a catalyst inside a cluster falls.

[0007] Conversely, if the degree of condensation is small, space formed between clusters becomes small, it will become easy to expose a catalyst supported by catalyst particle on the other hand to this space, and a capacity factor's of a catalyst will improve. When operating said polymer electrolyte type electrochemical cell by low current density, from a reaction occurring easily inside a catalyst bed near the polymer electrolyte membrane. As opposed to Mandatory having improvement in a catalyst capacity factor near [polymer electrolyte membrane] this, in order to obtain high voltage, Since it is thought that the neighborhood of a charge collector in which it is located comparatively distantly [polymer electrolyte membrane / this] seldom contributes to a reaction in low current density, it is not necessary to take into consideration so much for improvement in a catalyst capacity factor, and a case where it operates with high current density is taken into consideration, It is necessary to mainly solve whether gas which supplies smoothly [how] reactant gas supplied from this charge collector side near the polymer electrolyte membrane, and generates it is discharged.

[0008] Therefore, this invention person made it possible to provide a polymer electrolyte type electrochemical cell corresponding to the above-mentioned purpose by adjusting these paying attention to the degree of condensation of a catalyst particle, i.e., particle diameter of a cluster, and concentration of ion-exchange resin which covers a catalyst particle, in order to solve these problems. As above-mentioned, a polymer electrolyte type electrochemical cell, especially a fuel cell, It laminates in order of an anode charge collector-anode catalyst layer-polymer-electrolyte-membrane-cathode catalyst bed-cathode charge collector, hydrogen gas and oxygen gas which are reactant gas are supplied to polymer electrolyte membrane through each catalyst bed from the anode charge collector and cathode charge collector side, respectively, and a gas reaction advances. In this case, if the degree of condensation of a catalyst particle near [near a near charge collector in which gas is supplied] the catalyst bed is enlarged, gas supplied greatly will move toward the polymer-electrolyte-membrane side easily, and space produced in a gap of particles will reach this film. That is, the gas permeation nature of a catalyst bed by the side of a charge collector becomes good. And near [polymer electrolyte membrane] this, the degree of condensation of a catalyst particle is low, that is, many catalyst particle surfaces are exposed, and a reaction advances equivalent to the former, or more than it. Although a steam generated by a reaction moves in said direction of a charge collector and it is discharged out of a system, since the degree of condensation of a catalyst particle near the charge collector is high also in this case, it is smoothly taken out out of a system.

[0009] In order to form inclination of the degree of condensation of a catalyst particle in the direction of a catalyst bed, When based on a filtration process, a solution which distributed a catalyst particle is neglected for a while on a charge collector, and after it makes said catalyst particle sediment automatically and the charge collector side raises density of cluster particles with large particle diameter, it is attained by making it unify by the conventional hot pressing etc.

Although time of natural sedimentation changes with particle diameter, required cluster particle size distribution, the amounts of ion-exchange resin, etc. of a catalyst particle, in distribution by 1 micrometer of mean particle diameter of the range of 0.2-2 micrometers, it is desirable to consider it as 5 minutes or more, for example. Suitable cluster distribution for a thickness direction of a catalyst bed is it hard to be formed to be less than 5 minutes. Thus, besides forming condensation degree distribution, a catalyst bed of two sheets from which the degree of condensation differed mutually can be laminated, and a catalyst bed of one sheet can also be formed by the usual hot pressing etc.

[0010]In this invention, besides forming inclination of the degree of condensation of a catalyst particle in this way, when covering ion-exchange resin to a catalyst particle, that from which the amount of ion-exchange resin differs can be created, and a concentration gradient of ion-exchange resin can also be formed in an electrode thickness direction using these. If concentration of said ion-exchange resin (for example, trade name Nafion of Du Pont) is high, movement of a proton will arise easily, but gas permeation nature becomes low, if concentration is conversely low, it will be hard to produce movement of a proton, but gas permeation nature becomes good.

[0011]Therefore, if ion-exchange resin concentration by the side of polymer electrolyte membrane is made high and ion-exchange resin concentration by the side of a charge collector is made low, ion conductivity can provide a fuel cell which was highly excellent also in gas permeation nature like a case where it is the fuel cell with which the degree of condensation of a catalyst particle was adjusted.

[0012]When operating polymer electrolyte type electrochemical cells, such as a fuel cell, gas diffusion in an electrode becomes rate-limiting in a high current density field, On the cathode pole, there are especially many yields of produced water in a field of high current density, it is required to discharge this effectively and to introduce oxygen gas effectively to a catalyst surface, and this is attained by electrode of this invention. Promoting supply and discharge of gas in a low current density field similarly makes it possible to take out high power.

[0013]In an electrode of this invention, an electric conductive material currently used conventionally, for example, carbon paper, a porous carbon nonwoven fabric, carbon textiles, a carbon plate, etc. can be used as a charge collector, and water-repellent treatment of these may be carried out. It is preferred to also make into conventional carbon black catalyst support which makes a catalyst support, in addition a carbon single fiber may be made to support and what used both this fiber and a carried catalyst is contained in this invention. The precious metals, such as platinum, palladium, and a ruthenium, can be used as a catalyst in an electrode of this invention. Perfluorocarbon sulfonic acid etc. are used as ion-exchange resin. Water-repellent resin, such as Teflon (trade name), may be made intermingled in an electrode catalyst layer.

[0014]Drawing 2 and 3 illustrate the fine structure of a polymer electrolyte type electrochemical cell concerning this invention, and illustrate a respectively separate mode. Laminate a fuel cell of drawing 2 in order of the anode charge collector 11-anode catalyst layer 12-polymer-electrolyte-membrane 13-cathode catalyst bed 14-cathode charge collector 15, and it is constituted, The particle diameter of both the catalyst beds 12 and 14 is [about 16 the condensed anode charge collector 11 and about 15 cathode charge collector catalyst particle] large, and they are adjusted, respectively as about 13 polymer electrolyte membrane catalyst particle condensed 16' so that the particle diameter may become small.

[0025]Laminate a fuel cell of drawing 3 in order of the anode charge collector 21-anode catalyst layer 22-polymer-electrolyte-membrane 23-cathode catalyst bed 24-cathode charge collector 25, and it is constituted, The layer 22a of two sheets constituted by the catalyst particle 26 in which catalyst particles with which ion-exchange resin was covered condensed both the catalyst beds 22 and 24, respectively, 22b, and 24a and 24b are laminated by adhesion etc., and it is constituted, the layers 22a and 24a nearer to the anode charge collector 21 and the cathode charge collector 25 have lower ion-exchange resin concentration, and it is adjusted as the layers 22b and 24b near the polymer electrolyte membrane 25 so that ion-exchange resin concentration may become high.

[0026]

[Working example]Next, although an embodiment of polymer electrolyte type electrochemical cell manufacture concerning this invention is indicated, this example does not limit this invention.

[Work example 1]A carried catalyst which performed reduction processing and made 30weight % of platinum support after surface area made a carbon particle which is 300 m²/g impregnate chloroplatinic acid solution (platinum concentration of 5g/l.). What distributed a carbon single fiber with an average diameter of 1 micrometer so that a single fiber might be 25 weight % by a carbon ratio to carrier carbon of said carried catalyst. It was made to distribute by an ultrasonic homogenizer in the Nafion (trade name) solution containing solid content of quantity which will be 40 weight % to this amount of total carbon, and disintegration was dried and carried out, stirring. This powder was neglected for 5 minutes and made to sediment automatically on carbon paper which carried out re dispersion for 10 minutes, and carried out water-repellent treatment into ethanol using an ultrasonic homogenizer. Then, as it was, suction filtration was carried out, the hotpress of the solution was carried out, it was bound with 130 **, and it was considered as a cathode terminal. an anode electrode is the above-mentioned process, make a carbon particle support platinum, and be involved Nafion -- it transferred on carbon paper which filtered and carried out water-repellent treatment of the solution distributed to ** ethanol, and the hotpress was carried out, and it bound with 130 **, and created by it. Each electrode was used as a cell of this example as sandwich structure which sandwiched an ion-exchange membrane (Nafion). [0027]

[Work example 2]It forms on carbon paper which carried out water-repellent treatment by suction filtration without making it distribute using an ultrasonic homogenizer and making powder prepared in Embodiment 1 sediment automatically. On it, suction filtration constituted an electrode, without forming powder which covered Nafion and making same dispersed solution sediment automatically so that a carried catalyst and Nafion might be set to carbon:Nafion =5:5, and a cell was constituted like Embodiment 1 using this electrode. [0028]

[Work example 3]A solution made to sediment automatically like Embodiment 1 was made to sediment automatically on carbon paper as it is, and it filtered, and also it filtered, without making same solution that is carbon:Nafion =5:5 sediment automatically on it, an electrode was constituted, and a cell was constituted like Embodiment 1 using this electrode. [0029]

[The comparative example 1] Except having carried out [not performing natural sedimentation] suction filtration, an electrode was produced on the same conditions as Embodiment 1, and a cell was constituted using this electrode. A quality assessment (current density obtained on different voltage) of each cell of Embodiments 1-3 and the comparative example 1 was performed on the following conditions. The result was shown in Table 1.

platinum holding amount: -- 2 mg/cm² cell temperature: -- 80 ** anode gas humidification temperature: -- 90 ** gas pressure: -- zero gas: -- hydrogen and oxygen [0030]Relation between current density in Embodiment 3 and cell voltage was shown in a graph which shows drawing 4 relation between current density in Embodiment 1, and cell voltage again at a graph shown in drawing 5.

[0031]

[Table 1]

	実施例 1	実施例 2	実施例 3	比較例 1
0.9 Vでの電流密度	9 mA/cm ²	9 mA/cm ²	16mA/cm ²	5 mA/cm ²
0.7 Vでの電流密度	1300mA/cm ²	1250mA/cm ²	1500mA/cm ²	1000mA/cm ²
0.5 Vでの電流密度	3000mA/cm ²	2300mA/cm ²	3000mA/cm ²	2000mA/cm ²

[0032]

[Effect of the Invention]This invention is laminated in order of an anode charge collector-anode catalyst layer-polymer-electrolyte-membrane-cathode catalyst bed-cathode charge collector. In the catalyst bed of the electrode for polymer electrolyte type electrochemical cells which

formed in layers the cluster particles which grow into catalyst support from the catalyst particle and ion-exchange resin which supported the catalyst. It is a polymer electrolyte type electrochemical cell (Claim 1) distributing said catalyst particle so that the particle diameter of said cluster of the small side near a charge collector may become large about the particle diameter of said cluster of the side near the polymer electrolyte membrane of at least one catalyst bed.

[0033]The capacity factor of a catalyst falls, while its gas permeation nature improves so that the particle diameter of the condensed catalyst particle is large, gas permeation nature falls so that it is conversely small, but the capacity factor of a catalyst improves. Therefore, if the small condensation catalyst particle of particle diameter is located near the polymer electrolyte membrane like this invention and the large condensation catalyst particle of particle diameter is located near the charge collector, The supply of reactant gas whose catalyst capacity factor near [which does not need improvement in gas permeation nature so much] the polymer electrolyte membrane whose gas permeation nature of the catalyst bed near [improvement in a catalyst capacity factor is not required for] the charge collector improved, and improved, and discharge of production gas are easy, and electrochemical cells, such as a high-output fuel cell obtained, can be provided.

[0034]This invention is the electrochemical cell to which the polymer-electrolyte-membrane side made high concentration of the ion-exchange resin which covers the catalyst particle which constitutes the catalyst bed of the electrochemical cell which laminates an anode charge collector-anode catalyst layer-polymer-electrolyte-membrane-cathode catalyst bed-cathode charge collector to the 2nd (Claim 2). This ion-exchange resin tends to move a proton, so that concentration is high, that is, a reaction advances easily, and gas permeation nature becomes good, so that it is low. Therefore, if the height of the concentration of this compound has the same effect as the size of the particle diameter of the condensation catalyst particle of the 1st invention to the performance of a fuel cell, the concentration is made high as the polymer-electrolyte-membrane side and the concentration is made low as the charge collector side, Supply of reactant gas and discharge of production gas are easy like the 1st invention, and electrochemical cells, such as a high-output fuel cell obtained, can be provided.

[0035]After the electrochemical cell concerning said 1st invention locating the dispersion liquid of a catalyst particle on at least one charge collector of each and making it sediment automatically, it can be filtered and manufactured on this charge collector (Claim 3). That is, it becomes possible to manufacture the electrochemical cell which has the performance which was superior to the cell conventional only by adding the very easy technique of neglecting liquid before filtration. The electrochemical cell concerning said 2nd invention produces several catalyst beds from which ion-exchange resin concentration differs, and can manufacture them from the catalyst bed which has ion-exchange resin of maximum concentration by laminating from the polymer-electrolyte-membrane side in order of concentration (Claim 4). Although this method requires time and effort from the method according to claim 3, the amount of the comparatively expensive ion-exchange resin used can be saved, and the maximum efficiency can be produced by use of this compound of the minimal dose.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a mimetic diagram about the principle and composition of a polyelectrolyte type fuel cell.

[Drawing 2]The outline sectional view showing the 1st mode of polymer electrolyte type Electrochemistry Sub-Division concerning this invention.

[Drawing 3]Similarly it is an outline sectional view about the 2nd mode.

[Drawing 4]The graph which shows the relation between current density and cell voltage to Embodiment 1.

[Drawing 5]The graph which shows the relation between current density and cell voltage to Embodiment 1.

[Explanations of letters or numerals]

11, 21 [... Cathode catalyst bed 15, 25 / ... Cathode charge collector 16, 16', 26 / ...
Condensation catalyst particle] ... Anode charge collector 12, 22 ... Anode catalyst layer 13, 23 ...
Polymer electrolyte membrane 14 and 24

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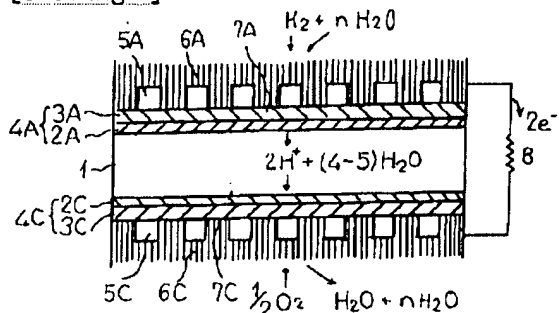
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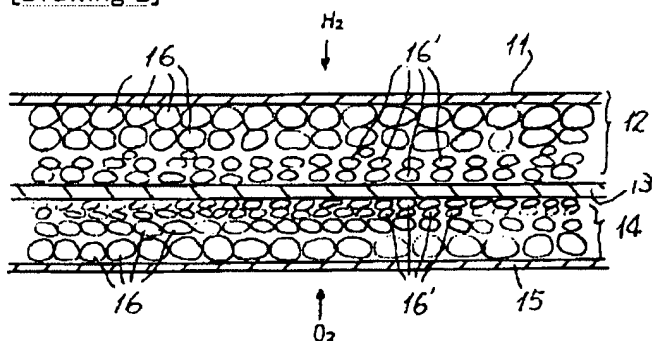
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DRAWINGS

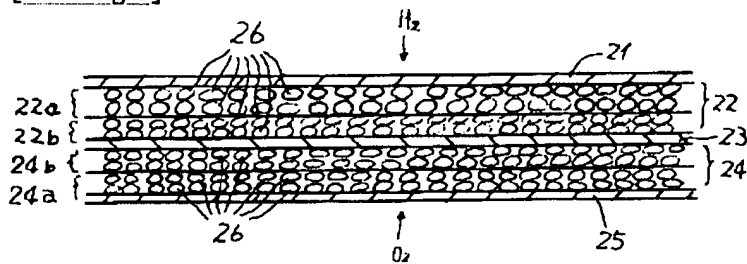
[Drawing 1]



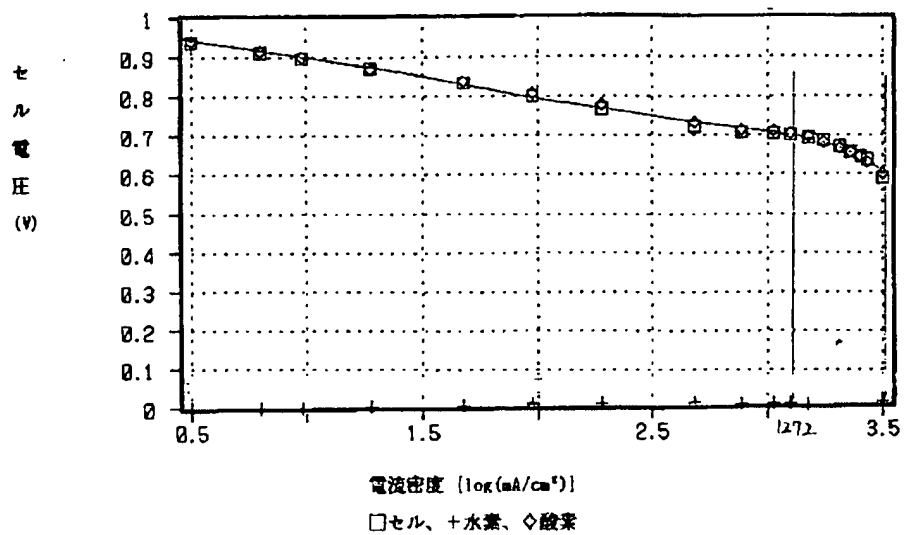
[Drawing 2]



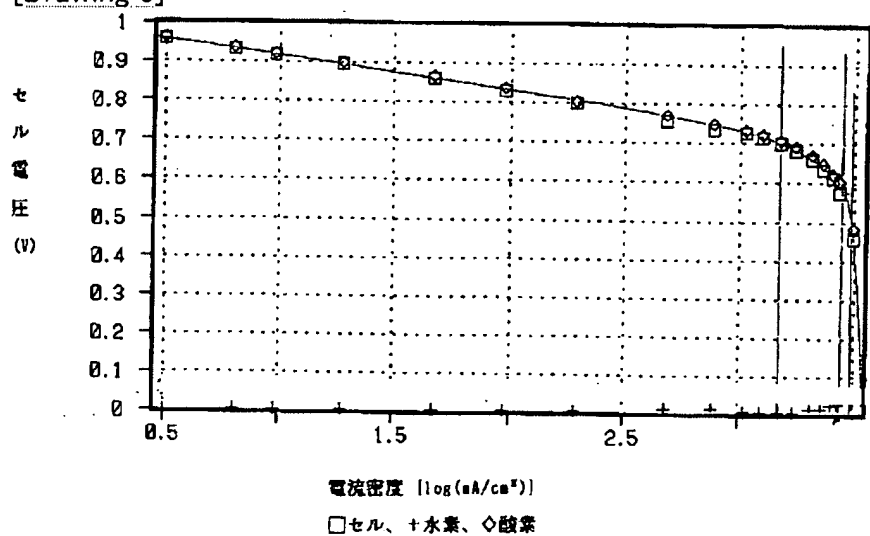
[Drawing 3]



[Drawing 4]



[Drawing 5]



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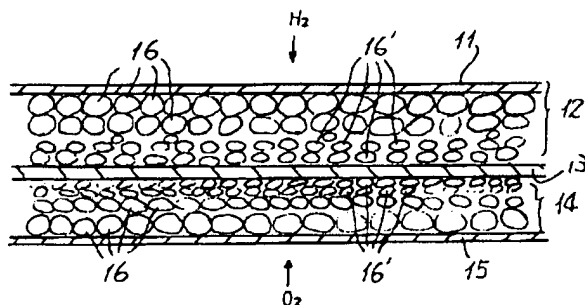
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(54)【発明の名称】 高分子電解質型電気化学セル及びその製造方法

(57)【要約】

【目的】 ガス透過性が高く、かつ高出力を得ることができる高分子電解質型電気化学セルを提供する。

【構成】 アノード集電体11-アノード触媒層12-高分子電解質膜13-カソード触媒層14-カソード集電体15の順に積層した電気化学セルの前記両触媒層の少なくとも一方の凝集した触媒粒子16、16'の粒径を高分子電解質膜に近づくほど小さくかつ集電体に近づくほど大きくなるよう分布させる。集電体に近い側ではガス透過性が優先され、高分子電解質膜に近い側では触媒の利用率が重視されるため、このように分布させることにより最高のガス透過性と触媒の利用率が得られる。



【特許請求の範囲】

【請求項1】 アノード集電体ーアノード触媒層ー高分子電解質膜ーカソード触媒層ーカソード集電体の順に積層して成り、触媒担体に触媒を担持した触媒粒子及びイオン交換樹脂より成るクラスター粒子を層状に形成した高分子電解質型電気化学セル用電極の触媒層において、少なくとも一方の触媒層の高分子電解質膜に近い側の前記クラスターの粒径を小さくかつ集電体に近い側の前記クラスターの粒径が大きくなるよう前記触媒粒子を分布させたことを特徴とする高分子電解質型電気化学セル。

【請求項2】 アノード集電体ーアノード触媒層ー高分子電解質膜ーカソード触媒層ーカソード集電体の順に積層して成り、触媒担体に触媒を担持した触媒粒子及びイオン交換樹脂より成るクラスター粒子を層状に形成した高分子電解質型電気化学セル用電極の触媒層において、少なくとも一方の触媒層の高分子電解質膜に近い側の前記イオン交換樹脂の濃度を高くかつ集電体に近い側のイオン交換樹脂の濃度を低くなるよう前記クラスター粒子を分布させたことを特徴とする高分子電解質型電気化学セル。

【請求項3】 アノード集電体ーアノード触媒層ー高分子電解質膜ーカソード触媒層ーカソード集電体の順に積層して成り、両触媒層が触媒担体に触媒を担持した触媒粒子及びイオン交換樹脂より成るクラスター粒子を層状に形成した高分子電解質型電気化学セル用電極の触媒層の製造方法において、少なくとも一方の各集電体上にイオン交換樹脂を被覆又は吸着させた触媒粒子クラスターの分散液を該集電体上に自然沈降濾過させた後に、アノード集電体ーアノード触媒層ー高分子電解質膜ーカソード触媒層ーカソード集電体の順に積層することを特徴とする高分子電解質型電気化学セルの製造方法。

【請求項4】 アノード集電体ーアノード触媒層ー高分子電解質膜ーカソード触媒層ーカソード集電体の順に積層して成り、触媒担体に触媒を担持した触媒粒子及びイオン交換樹脂より成るクラスター粒子を層状に形成した触媒層から成る高分子電解質型電気化学セル用電極の製造方法において、イオン交換樹脂濃度の異なる複数のクラスター粒子を作製し、最高濃度のイオン交換樹脂を有するクラスター粒子を前記高分子電解質膜側から濃度の高い順に層状に積層して少なくとも一方の触媒層を構成し、アノード集電体ーアノード触媒層ー高分子電解質膜ーカソード触媒層ーカソード集電体の順に積層することを特徴とする高分子電解質型電気化学セルの製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、反応ガスの供給及び生成ガスの排出を容易にし、実用域で得られる限界出力を向上させた高分子電解質型電気化学セル及びその製造方法に関する。

【0002】

【従来技術及び問題点】高分子電解質型電気化学セル例えば燃料電池は、リン酸型燃料電池と比較してコンパクトで高い電流密度を取り出せることから電気自動車、宇宙船用の電源として注目されている。又この分野の開発においても種々の電極構造や触媒作製方法、システム構成等に関する提案がなされている。図1は高分子電解質型燃料電池の原理及び構成を模式的に示すものであり、イオン交換膜1の一方面に、アノード側多孔質触媒層2Aとアノード側撥水性多孔質集電体層3Aを接合して成るアノード側ガス拡散電極4Aが、又他面にはカソード側多孔質触媒層2Cとカソード側撥水性多孔質集電体層3Cを接合して成るカソード側ガス拡散電極4Cが接合されている。アノード側のガス拡散電極4Aには反応ガス供給溝5Aを有するセパレータ6Aが接し、該セパレータ6Aの供給溝5A間に集電部7Aが形成されている。同様にカソード側のガス拡散電極4Cには反応ガス供給溝5Cを有するセパレータ6Cが接し、該セパレータ6Cの供給溝5C間に集電部7Cが形成されている。両集電部6A、46間を負荷8を有する導線で接続し、アノード側に水素、カソード側に酸素を供給すると前記負荷8から電力を取り出すことができる。

【0003】このような電気化学セル用電極の電極触媒層の担体としてカーボン粒子が使用され、このカーボン粒子とイオン交換樹脂を混合しホットプレス等により結着して電極触媒層が形成される。このように形成された電極触媒層はカーボン粒子が球形であるため隙間無く充填され、しかもホットプレスにより互いに強固に密着して密度が高くなっているため、ガスの流通路が少なく、従って原料ガスが電極触媒層中を拡散して反応点に到達しにくく更に反応後の生成ガスの排出も円滑に行いにくいという欠点がある。そのため原料ガスの供給が更に行いにくくなり、電極触媒層での反応効率が大幅に低下し、理論的な最大出力を大きく下回るエネルギーしか取り出せないという問題点が生じている。

【0004】

【発明の目的】本発明は上記問題点に鑑み、反応ガスの供給及び生成ガスの排出を円滑に行なうとともに、最大の出力が得られるような高分子電解質型電気化学セル用電極及びその製造方法を提供することを目的とする。

【0005】

【問題点を解決するための手段】本発明は、集電体、触媒層及び高分子電解質膜を積層して成る高分子電解質型電気化学セルの触媒が凝集したクラスターの粒径を集電体側に近づくほど大きく、高分子電解質膜側に近づくほど小さくし、あるいは前記触媒を被覆するイオン交換樹脂の濃度を集電体側に近づくほど小さく、高分子電解質膜側に近づくほど大きくした高分子電解質型電気化学セル及びその製造方法である。

【0006】以下、本発明の詳細について説明する。本発明は、第1に触媒層を通して行なわれる反応ガスの供

給及び生成ガスの排出を円滑に行なうことを意図し、第2にアノードガス及びカソードガス間の反応を促進することを意図する。触媒層は、微細な触媒を触媒担体に担持した多数の触媒粒子及びイオン交換樹脂から成るが、触媒粒子は相互に凝集してクラスター（凝集体）を形成している。凝集度が大きいほどつまりクラスターの粒径が大きいほど、クラスター間に形成される空間は大きくなり、一方触媒粒子に担持された触媒が該空間に露出しくくなりクラスター内部の触媒の利用率は低下する。

【0007】逆に凝集度が小さいと、クラスター間に形成される空間は小さくなり、一方触媒粒子に担持された触媒が該空間に露出しやすくなり触媒の利用率は向上する。前記高分子電解質型電気化学セルを低電流密度で運転する場合に、反応が高分子電解質膜近傍の触媒層内部で起こりやすいことから、高い電圧を得るために該高分子電解質膜近傍では触媒利用率の向上が必須があるのに対し、該高分子電解質膜から比較的遠く位置する集電体近傍は低電流密度での反応にあまり寄与しないと考えられることから触媒利用率の向上にはさほど考慮する必要はなく、高電流密度で運転する場合を考慮して、該集電体側から供給される反応ガスを如何に円滑に高分子電解質膜近傍に供給し、かつ生成するガスを排出するかを主として解決する必要がある。

【0008】従って本発明者は、これらの問題点を解決するために、触媒粒子の凝集度つまりクラスターの粒径と、触媒粒子を被覆するイオン交換樹脂の濃度に着目し、これらを調節することにより、前述の目的に合致した高分子電解質型電気化学セルを提供することを可能にした。前述の通り高分子電解質型電気化学セル特に燃料電池は、アノード集電体ーアノード触媒層ー高分子電解質膜ーカソード触媒層ーカソード集電体の順に積層して成り、反応ガスである水素ガスと酸素ガスはそれぞれアノード集電体側及びカソード集電体側からそれぞれの触媒層を通して高分子電解質膜へ供給されガス反応が進行する。この際に、ガスが供給される側の集電体に近い触媒層近傍の触媒粒子の凝集度を大きくしておくこと、粒子の間隙に生ずる空間が大きく供給されたガスが容易に高分子電解質膜側に向かって移動して該膜に到達する。つまり集電体側の触媒層のガス透過性が良好になる。そして該高分子電解質膜近傍では触媒粒子の凝集度が低く、つまり多くの触媒粒子表面が露出して反応が従来と同等又はそれ以上に進行する。反応により生成する水蒸気は前記集電体方向に移動し系外に排出されるが、この場合にも集電体近傍の触媒粒子の凝集度が高いため円滑に系外に取り出される。

【0009】触媒層方向に触媒粒子の凝集度の勾配を形成するためには、濾過法による場合には、触媒粒子を分散した溶液を集電体上に暫く放置し、前記触媒粒子を自然沈降させて集電体側ほど粒子径の大きいクラスター粒子の密度を上昇させた後に、従来のホットプレス法等に

より一体化させることにより達成される。自然沈降の時間は、触媒粒子の粒径、必要なクラスター粒径分布やイオン交換樹脂量等により変化するが、例えば平均粒径が $1\mu\text{m}$ で $0.2\sim 2\mu\text{m}$ の範囲の分布の場合は5分以上とすることが望ましい。5分未満であると触媒層の厚み方向に適当なクラスター分布が形成されにくい。このように凝集度分布を形成する以外に、互いに凝集度の異なった2枚の触媒層を積層し、通常のホットプレス法等により1枚の触媒層を形成することもできる。

【0010】本発明では、このように触媒粒子の凝集度の勾配を形成する以外に、触媒粒子にイオン交換樹脂を被覆する際にイオン交換樹脂量の異なるものを作成し、これらを用いて電極厚み方向にイオン交換樹脂の濃度勾配を形成することもできる。前記イオン交換樹脂（例えばデュボン社の商品名ナフィオン）の濃度が高いとプロトンの移動が容易に生じるがガス透過性が低くなり、逆に濃度が低いとプロトンの移動は生じにくいガス透過性は良好になる。

【0011】従って高分子電解質膜側のイオン交換樹脂濃度を高くし、集電体側のイオン交換樹脂濃度を低くすると、触媒粒子の凝集度が調節された燃料電池の場合と同様にイオン伝導性が高くかつガス透過性にも優れた燃料電池を提供できる。

【0012】燃料電池等の高分子電解質型電気化学セルを作動させる場合、高電流密度領域では電極中のガス拡散が律速となり、特にカソード極では高電流密度の領域で生成水の発生量が多く、これを効果的に排出して触媒表面へ酸素ガスを効果的に導入することが必要で、これが本発明の電極により達成される。同様に低電流密度領域でもガスの供給及び排出を促進することは高出力を取り出すことを可能にする。

【0013】本発明の電極では、集電体として従来使用されている電気伝導性材料、例えばカーボンペーパー、多孔質カーボン不織布、カーボン織物、カーボンプレート等を使用でき、又これらは撥水処理されたものであっても良い。触媒を担持させる触媒担体も従来のカーボンブラックとするのが好ましく、この他にカーボン単繊維に担持させても良く、本発明では該繊維と担持触媒の両方を用いたものが含まれる。又本発明の電極における触媒としては、白金、パラジウム、ルテニウム等の貴金属を使用できる。又イオン交換樹脂としてはパーフルオロカーボンスルホン酸等が用いられる。又電極触媒層中にテフロン（商品名）等の撥水性樹脂を混在させても良い。

【0014】図2及び3は、本発明に係わる高分子電解質型電気化学セルの微細構造を例示するもので、それぞれ別個の態様を例示する。図2の燃料電池は、アノード集電体11ーアノード触媒層12ー高分子電解質膜13ーカソード触媒層14ーカソード集電体15の順に積層して構成され、両触媒層12、14はそれぞれ、アノード集電体11及び

カソード集電体15近傍の凝集した触媒粒子16ほどその粒径が大きく、高分子電解質膜13近傍の凝集した触媒粒子16'ほどその粒径が小さくなるよう調節されている。

【0025】又図3の燃料電池は、アノード集電体21ーアノード触媒層22ー高分子電解質膜23ーカソード触媒層24ーカソード集電体25の順に積層して構成され、両触媒層22、24はそれぞれ、イオン交換樹脂が被覆された触媒微粒子が凝集した触媒粒子26により構成された2枚の層22a、22b及び24a及び24bを接着等により積層して構成され、アノード集電体21及びカソード集電体25に近い層22a及び24aほどイオン交換樹脂濃度が低く、高分子電解質膜25に近い層22b及び24bほどイオン交換樹脂濃度が高くなるよう調節されている。

【0026】

【実施例】次に本発明に係わる高分子電解質型電気化学セル製造の実施例を記載するが、本実施例は本発明を限定するものではない。

【実施例1】表面積が $300 \text{ m}^2/\text{g}$ であるカーボン粒子に塩化白金酸水溶液（白金濃度 $5 \text{ g}/\text{リットル}$ ）を含浸させた後、還元処理を行って30重量%の白金を担持させた担持触媒と、平均直径 $1 \mu\text{m}$ のカーボン単繊維を、前記担持触媒の担体カーボンに対しカーボン比で単繊維が25重量%となるように分散させたものと、更に該トータルカーボン量に対して40重量%となる量の固形分を含むナフィオン（商品名）溶液中に超音波ホモジナイザで分散させ、攪拌しながら乾燥して粉末化した。この粉末を超音波ホモジナイザを使用してエタノール中に10分間再分散し、撥水化处理したカーボンペーパー上に5分間放置し、自然沈降させた。その後、そのまま溶液を吸引、濾過して 130°C でホットプレスして結着しカソード電極とした。アノード電極は上記工程で、カーボン粒子に白金を担持させナフィオンを絡めてエタノールに分散した溶液を濾過して撥水化处理したカーボンペーパー上に転写し、 130°C でホットプレスし結着して作成した。各々

の電極をイオン交換膜（ナフィオン）を挟んだサンドイッチ構造として本実施例の電池とした。

【0027】

【実施例2】実施例1で調製した粉末を、超音波ホモジナイザを使用して分散させ自然沈降させずに吸引濾過により撥水化处理したカーボンペーパー上に形成し、更にその上に、担持触媒とナフィオンをカーボン：ナフィオン＝5：5となるようにナフィオンを被覆した粉末を形成して同様の分散溶液を自然沈降させずに吸引ろ過により電極を構成し、この電極を使用して実施例1と同様にして電池を構成した。

【0028】

【実施例3】実施例1と同様に自然沈降させた溶液をそのままカーボンペーパー上に自然沈降させて濾過し、更にその上にカーボン：ナフィオン＝5：5である同様の溶液を自然沈降させずに濾過して電極を構成し、この電極を使用して実施例1と同様にして電池を構成した。

【0029】

【比較例1】自然沈降を行わず吸引濾過したこと以外は実施例1と同一条件で電極を作製し、該電極を使用して電池を構成した。実施例1～3及び比較例1の各電池の性能評価（異なった電圧で得られる電流密度）を次の条件で行った。その結果を表1に示した。

白金担持量： $2 \text{ mg}/\text{cm}^2$

セル温度： 80°C

アノードガス加湿温度： 90°C

ガス圧力：大気圧

ガス：水素及び酸素

【0030】実施例1における電流密度とセル電圧の関係を図4に示すグラフに、又実施例3における電流密度とセル電圧の関係を図5に示すグラフに示した。

【0031】

【表1】

	実施例1	実施例2	実施例3	比較例1
0.9 Vでの電流密度	$9 \text{ mA}/\text{cm}^2$	$9 \text{ mA}/\text{cm}^2$	$16 \text{ mA}/\text{cm}^2$	$5 \text{ mA}/\text{cm}^2$
0.7 Vでの電流密度	$1300 \text{ mA}/\text{cm}^2$	$1250 \text{ mA}/\text{cm}^2$	$1500 \text{ mA}/\text{cm}^2$	$1000 \text{ mA}/\text{cm}^2$
0.5 Vでの電流密度	$3000 \text{ mA}/\text{cm}^2$	$2300 \text{ mA}/\text{cm}^2$	$3000 \text{ mA}/\text{cm}^2$	$2000 \text{ mA}/\text{cm}^2$

【0032】

【発明の効果】本発明は、アノード集電体ーアノード触媒層ー高分子電解質膜ーカソード触媒層ーカソード集電体の順に積層して成り、触媒担体に触媒を担持した触媒粒子及びイオン交換樹脂より成るクラスター粒子を層状に形成した高分子電解質型電気化学セル用電極の触媒層において、少なくとも一方の触媒層の高分子電解質膜に近い側の前記クラスターの粒径を小さくかつ集電体に近い側の前記クラスターの粒径が大きくなるよう前記触媒粒子を分布させたことを特徴とする高分子電解質型電気

化学セル（請求項1）である。

【0033】凝集した触媒粒子の粒径は大きいほどガス透過性が向上する反面、触媒の利用率が低下し、逆に小さいほどガス透過性は低下するが、触媒の利用率は向上する。従って本発明のように高分子電解質膜の近傍に粒径の小さい凝集触媒粒子を位置させ、集電体の近傍に粒径の大きい凝集触媒粒子を位置させると、触媒利用率の向上が必要でない集電体近傍の触媒層のガス透過性が向上し、ガス透過性の向上をさほど必要としない高分子電解質膜近傍の触媒利用率が向上した、反応ガスの供給及

び生成ガスの排出が容易で、高出力の得られる燃料電池等の電気化学セルを提供できる。

【0034】本発明は、第2に、アノード集電体—アノード触媒層—高分子電解質膜—カソード触媒層—カソード集電体を積層して成る電気化学セルの触媒層を構成する触媒粒子を被覆するイオン交換樹脂の濃度を高分子電解質膜側ほど高くした電気化学セルである（請求項2）。このイオン交換樹脂は濃度が高いほどプロトンが移動しやすく、つまり反応が進行しやすく、低いほどガス透過性が良好になる。従って該化合物の濃度の高低は、燃料電池の性能に対して、第1の発明の凝集触媒粒子の粒径の大小と同様の効果を有し、高分子電解質膜側ほどその濃度を高くし、集電体側ほどその濃度を低くすると、第1の発明と同様に反応ガスの供給及び生成ガスの排出が容易で、高出力の得られる燃料電池等の電気化学セルを提供できる。

【0035】前記第1の発明に係わる電気化学セルは、少なくとも一方の各集電体上に触媒粒子の分散液を位置させ自然沈降させた後に該集電体上に濾過して製造できる（請求項3）。つまり濾過の前に液を放置するという極めて簡単な手法を追加するのみで従来のセルより優れた性能を有する電気化学セルを製造することが可能になる。又前記第2の発明に係わる電気化学セルは、イオン

交換樹脂濃度の異なる複数の触媒層を作製し、最高濃度のイオン交換樹脂を有する触媒層から濃度順に高分子電解質膜側から積層することにより製造できる（請求項4）。この方法は請求項3に記載の方法より手間が掛かるが、比較的高価なイオン交換樹脂の使用量を節約し、最小量の該化合物の使用により最大限の効率を生じさせることができる。

【図面の簡単な説明】

【図1】 高分子電解質型燃料電池の原理及び構成を模式図。

【図2】 本発明に係わる高分子電解質型電気化学の第1の態様を示す概略断面図。

【図3】 同じく第2の態様を概略断面図。

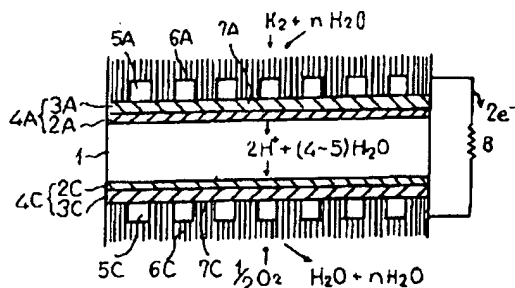
【図4】 実施例1に電流密度とセル電圧の関係を示すグラフ。

【図5】 実施例1に電流密度とセル電圧の関係を示すグラフ。

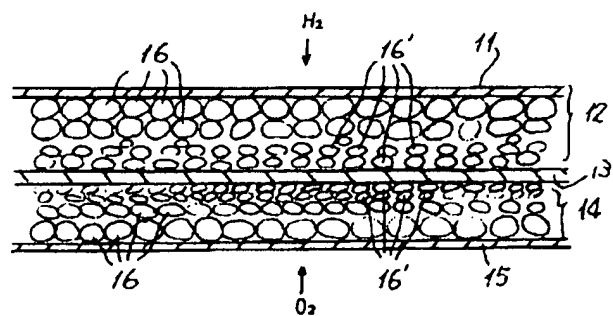
【符号の説明】

11、21・・・アノード集電体 12、22・・・アノード触媒層 13、23・・・高分子電解質膜 14、24・・・カソード触媒層 15、25・・・カソード集電体 16、16'、26・・・凝集触媒粒子

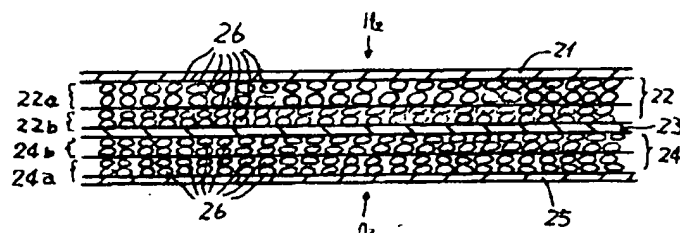
【図1】



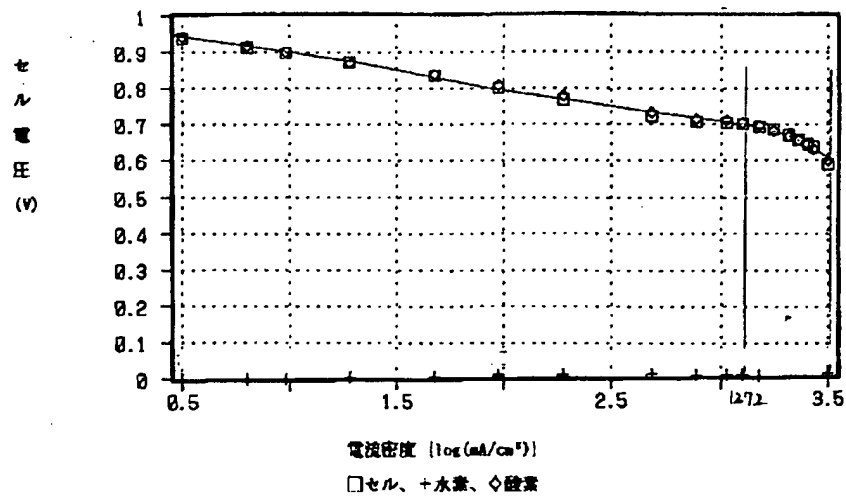
【図2】



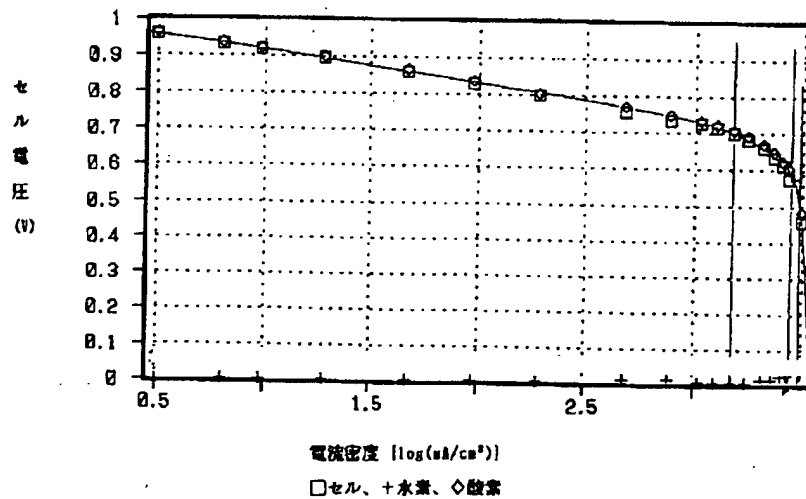
【図3】



【図4】



【図5】



フロントページの続き

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